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Synthesis and colloidal-chemical properties of manganese dioxide hydrosols synthesized in the presence of sodium thiosulfate

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Abstract. In this paper, the possibility of obtaining manganese dioxide hydrosols by condensation in the presence of sodium thiosulfate is considered. The main properties of hydrosols, including particle size and shape, phase composition, electrophoretic mobility, and the pH range of the dispersion medium in which sols are aggregatively stable, are determined. The sol coagulation thresholds in the presence of potassium chloride, sodium sulfate, and potassium sulfate were determined. It was found that the hydrosols coagulation is reversible. The nature of the aggregative stability of obtained manganese dioxide sols is discussed.

1 Introduction

In the chemical and metallurgy industries, manganese dioxide is often used as a catalyst. It is also used for wastewater treatment from organic pollutants [1-3], among them phenols [4]. Special attention is paid to the catalysts applying. At the same time, the size and state of the particles that are deposited on the carrier usually determine these catalysts activity. The sol-gel method is one of the generally accepted methods to create a system with the targeted properties.

Traditionally, potassium permanganate reduces by various reducing agents to obtain manganese dioxide from aqueous solutions; in this study, reactions with sodium thiosulfate were used. It is possible to regulate the properties of thin layers that form on the surface of the carrier, thanks to numerous options for choosing conditions for the synthesis, deposition, and heat treatment of already formed solid nanoparticles.

The purpose of this study is to identify the main colloidal-chemical properties of manganese dioxide hydrosols, which are supposed to be used as precursors for the production of applied catalysts further. To obtain a high-quality product by this method, it is necessary to maintain a uniform distribution of components, which can be achieved only while maintaining the aggregate stability of sols.

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2 Material and Methods

Manganese dioxide hydrosol may be obtained by various redox reactions by condensation [5-9]. Based on literature data, potassium permanganate was chosen as a source of manganese [10]. Sodium thiosulfate was used as a reducing agent. The reaction by which MnO_2 sols are synthesized is shown below.

$$8KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 8MnO_2 + 3Na_2SO_4 + 2KOH + 3K_2SO_4 \quad (1)$$

In the synthesis of hydrosols, aqueous solutions of hydrochloric acid and potassium hydroxide were used to regulate the pH balance of the dispersion medium. Coagulation of the obtained hydrosols was studied in the presence of potassium sulfate, potassium chloride, sodium sulfate and manganese chloride. The pH was determined using the Hanna pH meter Checker1. Atomic absorption spectroscopy was used to determine the concentration. The measurements were carried out on the KVANT-2A equipment at the Center for collective use of Mendeleyev University of Chemical Technology of Russia. Using cuvettes of various thicknesses: 1, 3, 5.10 microns, optical density measurements were carried out on an FEC 56PM photocolorimeter in the wavelength range of 400-650 nm. The zeta potential was measured using a PHOTOCOR Compact-Z device using standard round cuvettes 15x45 mm in size with a volume of 4 ml [11, 12]. Determination of the sol particle size 10 minutes after the start of synthesis was carried out using the Nanotrac ultralaser particle size analyzer (INV No. 110 104 115 925) at the Center for collective use of Mendeleyev University of Chemical Technology of Russia.

3 Results and Discussion

The method described by A. I. Ivanets [10] was used for the synthesis of manganese dioxide. Synthesis conditions were chosen to obtain systems that maintained aggregate stability for several weeks [13, 14]. The synthesized sols contained 0.03% wt MnO_2, the pH of the dispersion medium was 5.5.

Table 1. The synthesis conditions and the main characteristics of the obtained hydrosols MnO_2.

Maximum concentration, % by weight. pH of the initial sol	pH of the initial sol	Particle size, nm
0.03	5.5	20-30

Figure 1 presents a histogram of the size distribution of sol particles 10 minutes after synthesis, which shows that the average hydrodynamic diameter of sol particles is 20-30 nm. Obtaining a hydrosol with the minimum particle sizes and the highest concentration can be carried out by this method. Therefore, a hydrosol synthesized by this method was used in the further experiments.

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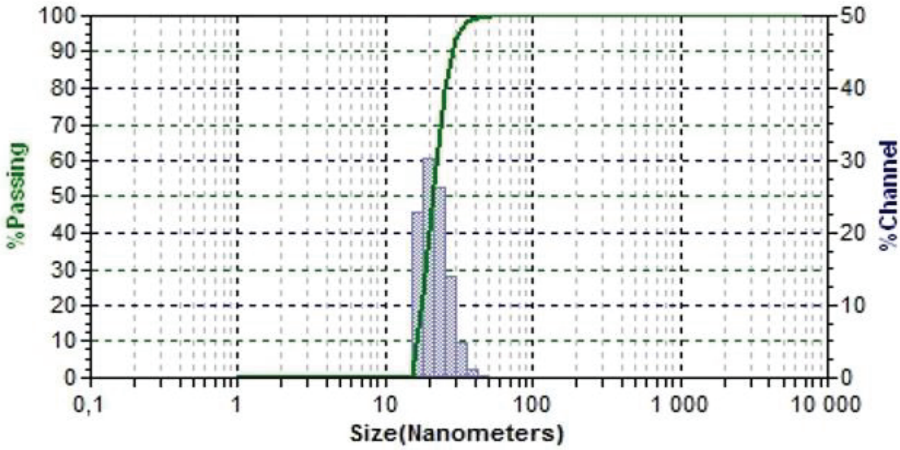

Fig. 1. Histogram of sol particle distribution by size 10 minutes after synthesis.

The most important property of hydrosols is the pH range in which they are aggregatively stable and sol stability in the presence of electrolytes. The dependence of the optical density on the pH values of manganese dioxide hydrosols is shown in Figure 2.

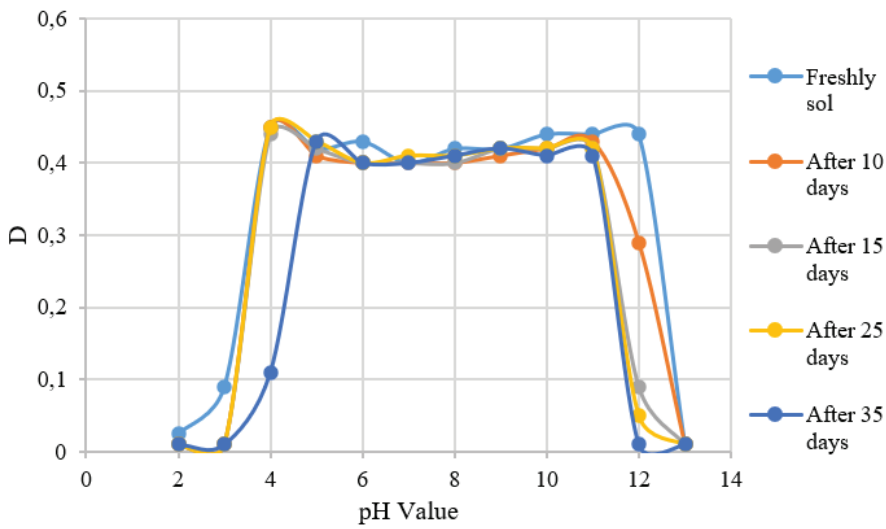

Fig. 2. Dependence of the sol optical density on the pH value at different exposure times.

The figure shows that freshly prepared sols are aggregatively stable at pH from 4 to 12. With a decrease in pH below 4, the decrease in optical density is associated with the dissolution of the solid phase. In the pH range exceeding 12, the decrease in optical density is associated with coagulation and particle deposition. It should be noted that after sol exposure, the interval during which the optical density remains constant decreases.

It is known that the structure of metal oxides and hydroxides DEL is largely determined by the pH value of the dispersion medium. The dependence of the ζ-potential on the pH value of the dispersion medium in the region of the aggregate stability of the studied system was obtained (Figure 3).

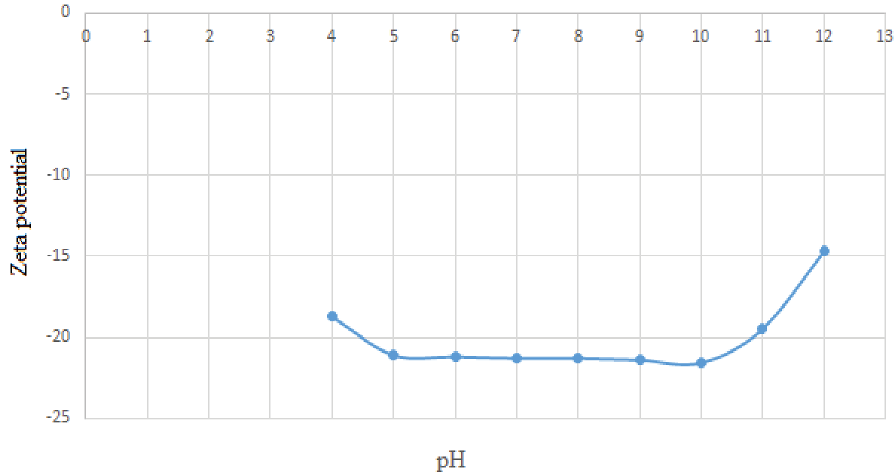

Fig. 3. Dependence of the ζ-potential on the pH value of the dispersion medium in the region of aggregative stability.

The figure shows that in the entire range of pH values, the particles are negatively charged and with increasing pH, the value of the ζ-potential decreases in absolute magnitude. It should also be noted that in the area of the hydrosol aggregative stability, i.e. at pH = 4-12, the value of the particles ζ-potential is –(20-25) mV. This means that the potential is low and hardly sufficient to ensure the aggregative stability of the sol. The above considerations are confirmed by the results obtained in the study of sol coagulation by electrolytes. The concentration of the electrolyte at which the rate of the process reached its maximum value was taken as the value of the coagulation threshold. The dependences of the values of the coagulation threshold for potassium sulfate, sodium sulfate and potassium chloride on the pH of the sol dispersion medium are shown in Figure 4.

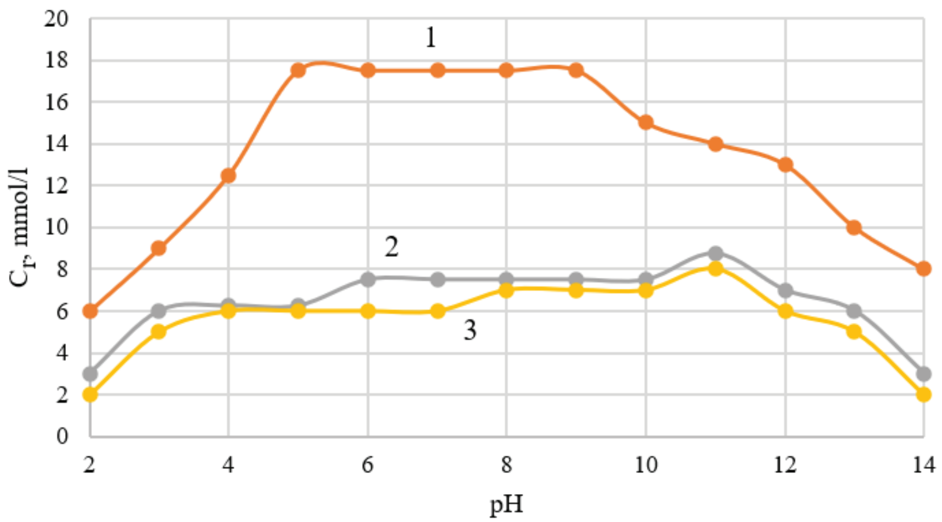

Fig. 4. Dependence of the coagulation thresholds C_r in the presence of various electrolytes on the pH of the dispersion medium. (1) KCl, (2) K_2SO_4, (3) Na_2SO_4.

As can be seen from this figure, the dependence of the coagulation thresholds on the dispersion medium pH has an extreme character, and the maximum on the presented curves

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corresponds to the range of pH values in which the sol is aggregatively stable in the absence of electrolytes (see Fig. 1).

In general, the obtained results show that not only the electrostatic factor of aggregative stability acts in the system under study. Coagulation thresholds were also obtained in the presence of potassium chloride, potassium sulfate, and sodium sulfate for sols of different concentrations (0.01-0.03% by weight). The coagulation thresholds were for KCl 17 mmol/L, for K_2SO_4 8 mmol/L and for Na_2SO_4 6 mmol/L. In the studied range of concentrations of the dispersed phase, the coagulation thresholds slightly depend on the concentration of sol, which characterizes the concentration coagulation caused by indifferent electrolytes. i.e., in its presence, the diffuse part of the sol DEL is mainly compressed.

Taking into account the fact that the contribution of the electrostatic factor is small, it was proposed that the coagulation of particles can occur through the layer of the dispersion medium. To verify this assumption, the optical density of coagulated sols was measured after intensive mixing. Electrolytes were added to the sol in concentrations equal to the coagulation threshold, kept for 10 minutes, then intensively mixed, and the optical density was measured. Sols without the addition of electrolyte were taken as a control. The coincidence of the optical densities with the control sols indirectly indicates reversible coagulation.

4 Conclusions

It is established that by direct condensation it is possible to obtain a stable manganese dioxide hydrosol with a particle size of 20-50 nm. In the absence of electrolytes, the hydrosol can be concentrated to 0.02 wt. %. A further increase in sol concentration becomes impossible due to the formation of a spatial structure. It is shown that the critical concentration of MnO_2 sol structure formation significantly depends on the ionic strength of the dispersion medium. Coagulation and structuring of MnO_2 hydrosols in the presence of an electrolyte are reversible due to the appearance of weak coagulation-type contacts between particles.

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